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THE USE OF BASIC NITROGENOUS COMPOUNDS IN THE LIQUEFACTION OF HIGH VOLATILE BITUMINOUS COAL

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THE USE OF BASIC NITROGENOUS COMPOUNDS
IN THE LIQUEFACTION OF HIGH-VOLATILE BITUMINOUS COAL

by

P.L. Sears* and J.A. McVeigh**

ABSTRACT

The effects of basic nitrogen-containing organic compounds in the dissolution of a Nova Scotia high-volatile "A" bituminous coal were studied. Experiments were carried out in tetralin and in anthracene oil, both at atmospheric pressure and in a closed autoclave. It was found that the extent of coal dissolution is strongly dependent on the amine used. Results are discussed with reference to the structures of these amines.

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UTILISATION DE COMPOSÉS DE BASE CONTENANT DE L'AZOTE
POUR LA LIQUÉFACTION D'UN CHARBON BITUMINEUX FORTEMENT VOLATIL

par

P.L. Sears* et J.A. McVeigh**

RÉSUMÉ

Le rapport porte sur les résultats d'une étude relative aux effets des composés organiques de base contenant de l'azote sur la dissolution d'un charbon bitumineux "A" fortement volatil en provenance de la Nouvelle-Écosse. Les essais ont été menés à l'aide d'huile anthracénique et de Tétraline à la pression atmosphérique de même que dans un autoclave fermé. Les résultats indiquent que l'importance de la dissolution du charbon repose fortement sur le type d'amine utilisé. Les résultats sont étudiés en fonction de la structure des amines.

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INTRODUCTION

It has long been known that certain basic nitrogen-containing organic compounds act as good coal solvents even under relatively mild conditions (1-6). The actual mechanism by which solvolysis takes place remains unclear, although a number of suggestions have been made as to the nature of the chemical interaction between the coal molecules and the nitrogen atom of the organic base. It appears that the basicity of an amine is not in itself a good indicator of its effectiveness in dissolving coal (2), but the usual measure of basicity (pK_a) refers to aqueous solution, and is not very appropriate under the conditions used for coal solubility experiments. Secondary and tertiary aliphatic amines are in general much poorer solvents than are the corresponding primary amines, indicating the possible importance of steric factors.

Heats of reaction of amines with aluminium trichloride have been measured (7), and correlate well with their relative coal dissolution abilities (7,3). Since these heats of reaction may be regarded primarily as the bond energies of the N-Al donor bonds in these Lewis adducts, it seems probable that lone pair donation by the nitrogen atom is an important feature of the reaction of coal with these amines. However, if the nature of the interaction is of the usual Lewis acid-Lewis base type, it remains to be determined what type of chemical group in the coal structure could act as the acid. There is some indication of the importance of hydrogen bonding, but again no clear suggestion emerges as to the specific type of moieties involved (3,5).

Later work indicates that other reactions do take place, with a more substantial bond developing between the nitrogen base and the coal molecules (6). In this case, tetrahydroquinoline (THQ) was reacted with two high-volatile bituminous coals, and the resulting extracts and insoluble materials were freed from excess THQ by vacuum distillation and acid extraction. It was found that the total amount of extract and soluble material was greater than the original amount of coal used, because of inclusion of THQ into the coal-derived material. It should be noted that THQ is a possible source of hydrogen as well as a

nitrogen-containing base, and that thus could react in ways which other bases could not.

In work presented at a meeting of the AIChE in 1982, reactions of model compounds were studied to attain some insight into possible mechanisms of the reactions of coal with nitrogen bases (8). These model systems often involved the reaction of THQ with a phenol or cyclic amide molecule. Some unusual reaction mechanisms were postulated for these reactions, but perhaps the most interesting result was that in many of the reactions the nitrogen base became attached to the framework of the molecule with which it was reacting. The resulting compound was of moderate molecular weight, but contained several highly polar groups and thus would be expected to have a high boiling point. This is consistent with experience of the use of THQ in coal liquefaction, where impressive yields of THF soluble material are somewhat offset by rather high boiling points and nitrogen contents.

Nevertheless, there remains some optimism that the goal of purely catalytic liquefaction by nitrogen compounds may be achievable (8). The recycle of high-boiling material in coal liquefaction processes often results in greater coal conversion. Specific experiments have been carried out (9) in which different fractions of coal-derived liquid were investigated separately. It was found that the fraction containing the basic nitrogen compounds was by far the most effective in coal liquefaction. It was also found that the solvating powers of the various fractions were not additive, and the effectiveness of the whole being considerably greater than the sum of its parts.

In a recently published paper on models of coal/solvent adducts it is again suggested that the primary bonding mechanism is some form of hydrogen bonding (10). This is based chiefly on indications that some systems in which quinoline is presumably hydrogen bonded to other material are rather reluctant to give up their quinoline under vacuum drying

conditions. However, this conclusion is not supported by the results obtained by Hausigk et al., who found that solvent remained incorporated into the coal-derived material even after hydrochloric acid extraction (6). Hydrogen bonded complexes would not be expected to resist this.

In this work the solubility of a high-volatile "A" bituminous Nova Scotia coal was studied, using tetralin and anthracene oil as solvents and various simple nitrogen-containing bases as additives. The objective was to determine whether any of these nitrogen compounds would act as catalysts for coal dissolution. Experiments were carried out in glass equipment at 1 atm, and in an autoclave where the pressure was allowed to rise to the vapour pressure of the reactants. An inert atmosphere was used throughout.

EXPERIMENTAL

A Nova Scotia hv "A" bituminous coal, with a volatile material content of approximately 31 wt % was used. Analytical details are given in Table 1. Immediately after removal from the mine, the coal was saturated with water to help prevent oxidation. The coal was ground to minus 200 mesh (minus $74\mu\text{m}$) and stored in plastic bags.

In this work, the conversion of coal was defined as the amount of coal rendered THF soluble, measured on a dry ash-free basis. This was determined by weighing the material remaining after exhaustive Soxhlet extraction of the reaction residue by THF. The amount of soluble material was found by difference. In some experiments it was also possible to separate and measure directly the amount of material rendered soluble.

Four sets of experiments were carried out to investigate the effects of different variables on the amount of coal solubilized. Two sets of runs were carried out in glass apparatus. The first was designed to ascertain the speed of reaction of the coal with tetralin and one

additive at the boiling point of the combined solvent at 1 atm. The second set of experiments was used to compare the effectiveness of different nitrogen-containing bases in conjunction with tetralin at atmospheric pressure.

At the temperatures used, oxygen was found to react quite rapidly with both coal and coal-derived material. Accordingly, all reactions were carried out under nitrogen. Atmosphere pressure reactions were carried out in a reflux apparatus, using 10 g of coal in 100 mL tetralin and 0.1 mol of nitrogen-containing additive. Blank runs were also carried out, in which no additive was used. No attempt was made to collect any gaseous material which might have been evolved. However, it is unlikely that any significant amount would be produced in the temperature range under study (157-213°C). The reaction mixture was refluxed for the required time and then filtered through a thoroughly dried, preweighed Soxhlet thimble. The thimble was then placed in a Soxhlet apparatus and exhaustively extracted with THF. This required several days.

When extraction was complete, as shown by the colour of the solvent leaving the thimble, the THF solution was added to the original liquid material, and the combined liquids were evaporated by rotary evaporator. This was carried out at 100°C under vacuum. Material remaining in the rotary evaporator was then dried at 150°C in a vacuum oven, and weighed. The Soxhlet thimbles with THF insoluble material were dried to constant weight under vacuum at 150°C, and the weight of insoluble material was then determined by difference. This procedure removes both tetralin and any nitrogen-containing base which is not bonded in some way to the solubilized coal.

Two sets of experiments were carried out in an autoclave. The first was identical to the second set of experiments in the glass

apparatus, except that the small size of the autoclave vessel necessitated a slight reduction of scale. A higher temperature than was attainable at atmospheric pressure was adopted for these experiments. The second set of autoclave experiments was similar, but anthracene oil was used instead of tetralin as the main solvent.

The autoclave was pressurized with argon before each run to check for leaks. If no pressure drop had occurred after several hours, the argon was vented, and heating begun. The pressure that developed in the vessel resulted from the vapour pressure of the reactants, with only a small contribution from the remaining argon. The material in the autoclave was stirred continuously, using a Magnedrive impeller. The reaction temperature was 350°C, and reactants were maintained at this temperature for 1 h. However, the thermal mass of vessel was such, that heating up and cooling took several hours. Every effort was made to ensure that these effects were consistent for all these experiments.

Product workup for the autoclave experiments was identical to that for those in glassware except that when anthracene oil was used it was not possible to separate the soluble coal-derived material from the liquid phase.

RESULTS AND DISCUSSION

LOW PRESSURE EXPERIMENTS

A set of four runs was carried out in tetralin, using piperidine as additive and a variable reaction time in order to ascertain the reaction time most appropriate for subsequent work with other variables. Reaction times of 15, 30, 60 and 120 min. were used and the amount of coal converted was determined for each. It became evident that piperidine was perhaps not the best additive to use for this as conversions were low (~5.5%) in every case. However, it was also clear that the amount of coal converted was not a strong function of reaction time, at least in the

range used here, and a time of 60 min. was selected for subsequent experiments.

A second set of experiments was then carried out using tetralin with a series of 9 different nitrogen-containing bases, and one blank run with no additive. Yields of soluble and insoluble materials are shown in Table 2. The mass of coal used for each experiment was 9.84 g (dry basis). It may immediately be seen that the sum of the amounts of soluble and insoluble materials derived is in general greater than this amount. It is also evident that the additives are ineffective in solubilizing the coal, as the percentage of coal converted is lower for every additive than it is in the blank run with no additive.

However, another variable is present here. The experiments were carried out under reflux, and the boiling point of the tetralin bulk solvent was considerably lowered in some cases by addition of the nitrogen base. The boiling point of the mixture shows some degree of correlation with the amount of coal rendered soluble (Fig. 1). This makes it difficult to draw any conclusions about the relative effectiveness of the different additives.

The elemental analyses of the products in Table 3 show a number of effects. The oxygen contents of the insoluble fractions and some of the soluble fractions are higher than that of the original coal. None of these fractions has a much lower oxygen content. This indicates that some oxidation had taken place in spite of the precautions. Sulphur contents are comparable with that of the coal for the insoluble fractions, and considerably lower for the soluble fractions. The overall sulphur mass balance is much better than the oxygen balance, as would be expected.

A problem with product analyses may also be seen here. The analyses for the samples of soluble material from the pyridine and 4-phenyl pyridine experiments show a marked shortfall in their totals, which are 86.8% and 88.2% respectively. The latter includes an estimate of 0.6% for sulphur. Both these figures should be close to 100%, and

the shortfalls indicate that the products had not been sufficiently dried before analysis. The samples lost material while awaiting analysis for C, H, N and O. This problem occurred elsewhere and was corrected, but in these two runs the product material was discarded too soon. An implication is that the weights of soluble material for these runs are high, by 10%. This does not affect the coal conversion figures as these were always determined from the weights of insoluble material.

The most interesting effect is shown by the nitrogen analyses. The total amount of nitrogen in the two fractions is shown in the last column of Table 4. When these figures are compared with the nitrogen content of the original coal it can be seen that nitrogen has been added to the coal-derived material. The amount added is not the same in each case however. In four of the runs, little or no addition has occurred. These are the blank run (no additive) and the runs where pyridine, 4-phenyl pyridine and 3,5 lutidine were used. Those runs where considerable addition occurred involved piperidine, four substituted piperidines, and a substituted pyrrolidine. In short, where aromatic compounds were used (pyridines), little or no addition took place, and where saturated compounds were used, the nitrogen content of the products was increased by 30-60%. The two instances where N-substituted compounds were used provide an interesting sidelight on the subject, as they show smaller increases in nitrogen content than are seen for the other saturated compounds.

If all the additional nitrogen is assumed to have been provided by incorporation of the entire additive molecule into the coal-derived products, then it is possible to evaluate the total amount of coal-derived product (including additive) which should result in each case. These quantities are shown in Table 2. Agreement with the actual total amounts is in most cases quite good.

Table 3 gives the nitrogen contents of the soluble and insoluble materials and shows that both classes of material exhibit an increase in

nitrogen content when the saturated additives are used, whereas in the other experiments, both classes have nitrogen contents comparable with that of the coal. It appears that the saturated compounds become strongly bonded to both fractions of the coal-derived material, whereas the aromatic compounds do not.

AUTOCLAVE EXPERIMENTS

To obtain a constant temperature for this type of experiment, and to avoid evaporation of the more volatile nitrogen compounds from the reaction vessel, it was necessary to enclose the reactants in a pressure vessel.

Reaction conditions were, as far as possible, similar to those used in the glassware, but the temperature was maintained at 350°C. Pressures attained were in the range 1 to 1.5 MPa. A reaction time of 1 h was used, but the slow heating required for the autoclave meant that the complete experiment took several hours. Results from these experiments are shown in Tables 5 and 6.

The conversions achieved in these runs were much higher than those for the atmospheric pressure runs. It may now be seen that the use of additive in some cases results in an appreciable increase in the amount of coal dissolved. However, there are large discrepancies in the mass balances for coal and coal products. Some oxidation of the samples is again evident, and the sulphur is now concentrated in the insoluble material. The sulphur contents of the soluble materials are a factor of about four lower than those of the insolubles. The nitrogen contents of these materials (Table 7) show the same type of effect as was seen for the atmospheric pressure runs, but in this case it is decidedly more pronounced. Again the nitrogen analyses have been used to predict total amounts of coal-derived material, including nitrogen-containing additive.

These quantities are shown in Table 5 for direct comparison with the actual amounts of material recovered. Agreement here is poorer than in the atmospheric pressure study.

The final series of experiments was carried out using anthracene oil as solvent for reactions in the autoclave. Anthracene oil was obtained from Crowley Tar Products Co. Inc., of New York. Analytical results for this oil are given in Table 8. Reaction conditions were the same as for the previous series, where tetralin had been used. Pressures reached were in the range 0.6 to 1.2 MPa. Results are shown in Table 9. Only the THF insoluble material could be weighed and analysed, since the soluble material could not be separated from the anthracene oil.

A number of effects are evident from the available data. First, the coal conversion figures show enormous variation with different additives. The additive does not always increase the amount of coal dissolved; in only two cases is a significant increase achieved: 2-methyl piperidine and N-methyl piperidine. Pyridine and 3,5-lutidine appear to have minimal effect, and the remaining three additives greatly reduce coal conversion. These are piperidine, 4-methyl piperidine and N-methyl pyrrolidine. The nitrogen contents of the insoluble materials are generally higher for those runs where additive is used, but this is not a large effect and nowhere does the content exceed 2%, as frequently occurs in the equivalent tetralin experiments (Table 6).

Since the pyridines have little effect, there is little that can be said about them. However the piperidines present an interesting picture. The position of any substituent methyl group appears to have a dramatic effect on the degree of coal conversion. With the methyl group on the nitrogen atom or in the 2 position, good conversion is achieved (75%), whereas when it is absent or in the 4 position, conversion is severely inhibited.

The obvious inference is that a steric effect is responsible for this, with the methyl group "blocking" the nitrogen to some extent when it is either on the nitrogen atom or the adjacent carbon atom. Such an effect might prevent undesirable condensation reactions of the additive with the coal. This conclusion is not supported by the result with N-methyl pyrrolidine. Here, although the nitrogen atom is "blocked" by a methyl group, the coal conversion is extremely poor. In this case the ring has only five members, rather than six as in the piperidines, but this difference would not normally be expected to make a difference this great to the chemistry involved. The contrast between the results for N-methyl pyrrolidine and N-methyl piperidine is unexpected.

CONCLUSIONS

1. This work gives some preliminary indications of the effects which occur when nitrogen-containing organic bases are used as additives in coal dissolution experiments carried out in tetralin or anthracene oil at 350°C. In tetralin the effect on the extent of dissolution is negligible, but the aliphatic bases tend to become incorporated into the products. In anthracene oil, marked effects, both beneficial and deleterious, are observed, but the tendencies of the nitrogen bases to become incorporated into the coal-derived material remain largely unknown because the soluble product material cannot be separated from the solvent.
2. Future work should extend the series of amines to determine the specific properties of these compounds which give rise to the phenomena discussed. Also, work should be done to determine how these amines react with the anthracene oil, and what basic and acidic compounds are in this material initially. Acid extractions should be used to determine the fate of the bases added to the anthracene oil

experiments. The effects of a hydrogen gas atmosphere and of higher temperatures should also be investigated.

REFERENCES

1. E. Fremy, C.R. Acad. Sci., Paris, 52, 114, (1861).
2. I.G.C. Dryden, Nature, 162, 959, (1948).
3. I.G.C. Dryden, Chem. and Ind., 30, 502, (1952).
4. C. Kroger, Erdol und Kohle, 9, 516, (1956).
5. A. Halleux and H. Tschamler, Fuel, 38, 291, (1959).
6. D. Hausigk, G. Kolling and F. Ziegler, Brennstoff Chemie, 56, 8, (1969)
7. M.H. Dilke, D.D. Eley and M.G. Sheppard, Trans. Faraday. Soc., 46, 261, (1950)
8. L.F. Atherton and C.J. Kulik, presentation to the 1982 AIChE meeting, Los Angeles.
9. F.J. Derbyshire, G.A. Odgerfer, L.R. Rudmick, P. Varghese and D.D. Whitehurst, (Mobil Oil Ltd.), EPRI contract No. 1665-1.
10. R.I. McNeil, D.C. Young and D.C. Cronauer, Fuel, 62, 806, (1983).

Table 1 - Analysis of original coal - high volatile "A" bituminous coal from
Devco's No. 26 colliery, harbour seam, Sydney Coalfield, Nova Scotia

Heat Value 32474 kJ/kg

Proximate Analysis (wt %)

	As received	Dry basis
Moisture	1.59	-
Volatile material	31.05	31.55
Fixed carbon	61.81	62.81
Ash	5.55	5.64

Ultimate Analysis (wt %)

	As received	Dry basis
C	78.49	79.76
H	4.79	4.68
N	1.50	1.52
O	6.50	5.17
S	1.58	1.61
Ash (by difference)	7.14	7.26

Table 2 - Yields of THF soluble and insoluble materials - low pressure experiments

Tetralin solvent 100 mL + 0.1 mol additive

Coal sample size 10 g = 9.84 g dry weight

9.29 daf weight

Nominal residence time at temperature:- 60 min.

Additive	Weight of additive (g)	THF soluble material (g)	THF insoluble material (g)	Total (g)	Total expected from nitrogen analyses (g)	Conversion (% daf)	Temp (°C)
None	-	2.76	7.15	9.91	-	29.0	209
Piperidine	8.5	1.13	9.06	10.19	10.40	8.4	169
Pyridine	7.9	1.53	8.91	11.53	9.98	10.0	171
3,5-Lutidine	10.7	2.27	7.90	10.17	9.95	20.9	196
4-Phenyl pyridine*	15.5	0.94	4.09	5.03	5.02	17.9	213
2-Methyl piperidine	9.9	1.51	9.13	10.64	10.49	7.7	174
N-Methyl piperidine	9.9	0.74	8.91	9.65	10.34	10.0	169
4-Methyl piperidine	9.9	1.16	9.11	10.27	10.48	7.9	179
3-Methyl piperidine	9.9	1.72	9.11	10.83	10.64	7.9	179
N-Methyl pyrrolidine	8.5	0.99	9.06	10.05	10.25	8.4	157

* Half-scale experiment

Table 3 - Product analyses - low pressure experiments

Additive	Analysis (wt %)										
	THF soluble material					THF insoluble material					
	C	H	N	O	S	C	H	N	O	S	Ash*
None	82.87	5.46	1.64	6.13	0.78	78.56	4.53	1.80	7.63	1.64	5.84
Piperidine	85.21	6.56	2.76	4.63	0.60	78.07	4.82	2.34	7.78	1.52	5.47
Pyridine	70.23	7.11	0.84	8.34	0.29	78.60	4.48	1.82	8.00	1.62	5.48
3,5-Lutidine	83.64	6.12	1.67	5.66	0.64	78.61	4.48	1.59	7.44	1.54	6.42
4-Phenyl pyridine	72.74	6.95	1.07	6.84	+	78.13	4.43	1.82	7.24	1.56	6.82
2-Methyl piperidine	84.53	6.84	2.24	4.90	0.63	78.58	4.71	2.28	7.81	1.55	5.07
N-Methyl piperidine	85.74	6.50	2.14	4.82	0.71	76.83	4.26	2.29	8.40	1.39	6.83
4-Methyl piperidine	83.87	6.99	2.18	4.64	+	76.99	4.18	2.37	8.28	1.10	7.08
3-Methyl piperidine	84.74	6.21	2.23	5.54	0.61	77.20	4.20	2.42	8.02	1.18	6.98
N-Methyl pyrrolidine	85.25	6.66	2.58	4.44	+	78.92	4.71	2.12	7.55	1.25	5.45

* By difference

+ Insufficient sample

Table 4 - Nitrogen contents of reaction products - low pressure experiments.

Additive	Nitrogen content (mg)		
	THF solubles	THF insolubles	Total
None	45	129	174
Piperdine	31	212	243
Pyridine	13	162	175
3,5 Lutidine	38	126	164
4-Phenyl pyridine*	10*	74.5*	84.5*
2-Methyl piperidine	34	208	242
N-Methyl piperidine	16	204	220
4-Methyl piperidine	25	216	241
3-Methyl piperidine	38	221	259
N-Methyl pyrrolidine	26	192	218
Unreacted coal	-	-	150

* Half-scale experiment

Table 5 - Yields of THF soluble and insoluble materials - low pressure experiments

Tetralin solvent 75 mL + 0.075 mol additive
 Coal sample size 7.5 g = 7.38 g dry weight
 6.96 g daf weight
 Residence time at 350°C: - 60 min.

Additive	Weight of additive (g)	THF soluble material (g)	THF insoluble material (g)	Total expected from nitrogen analyses (g)	Total (g)	Conversion (% daf)
None	-	3.11	4.23	-	7.34	45.3
Piperidine	6.375	4.35	4.16	8.19	8.51	46.3
Pyridine	5.925	4.44	3.98	7.59	8.42	48.9
3,5-Lutidine	8.025	3.20	3.99	7.54	7.19	48.7
4-Phenyl pyridine	11.625	3.03	3.82	7.8	6.85	51.2
2-Methyl piperidine	7.425	5.24	3.80	-	9.04	51.4
N-Methyl piperidine	7.425	3.87	4.02	8.00	7.89	48.3
4-Methyl piperidine	7.425	4.29	3.60	8.36	7.89	54.3
3-Methyl piperidine	7.425	5.38	3.53	8.62	8.91	55.3
N-Methyl pyrrolidine	6.375	4.37	4.00	8.25	8.37	48.6

Table 6 - Product analyses - autoclave experiments using tetralin as solvent

Additive	Analysis (wt %)										
	THF soluble material					THF insoluble material					
	C	H	N	O	S	C	H	N	O	S	Ash*
None	85.45	5.84	1.57	5.34	0.74	73.71	4.01	1.78	8.49	2.24	9.77
Piperidine	83.32	6.74	3.47	4.91	0.48	78.92	4.69	2.29	4.27	2.04	7.79
Pyridine	82.89	5.69	1.77	5.45	0.69	76.85	4.21	1.79	5.77	2.44	8.94
3,5-Lutidine	85.82	6.33	2.02	5.13	0.65	75.62	3.98	1.72	6.37	2.06	10.25
4-Phenyl pyridine	86.23	5.86	2.82	5.52	0.56	75.06	3.96	1.69	5.44	2.22	11.63
2-Methyl piperidine					0.44	74.72	4.05	2.21	7.29	2.03	9.7
N-Methyl piperidine	85.56	6.68	2.87	4.78	0.57	74.10	3.88	2.21	7.78	1.77	10.26
4-Methyl piperidine	84.37	6.97	3.87	4.60	0.52	73.60	3.70	2.35	7.65	1.80	10.90
3-Methyl piperidine	84.45	7.09	3.92	4.42	0.50	76.40	4.42	2.16	5.55	2.24	9.23
N-Methyl pyrrolidine	84.09	6.65	3.67	4.11	0.47	78.29	4.57	2.40	5.65	1.42	7.67

* By difference

Table 7 - Nitrogen contents of reaction products - autoclave experiments

Additive	Nitrogen content (mg)		
	THF solubles	THF insolubles	Total
None	49	75	124
Piperidine	151	95	246
Pyridine	79	71	150
3,5 Lutidine	65	68	133
4-Phenyl pyridine*	85	65	150
2-Methyl piperidine		84	
N-Methyl piperidine	111	89	200
4-Methyl piperidine	166	85	251
3-Methyl piperidine	211	76	287
N-Methyl pyrrolidine	160	96	256
Unreacted coal	-	-	112

Table 8 - Anthracene oil properties - analysis by Crowley Tar Products Inc.,
New York

Specific gravity @ 38/15.5°C	1.108
Water, %	0.0
Xylene insoluble, %	0.2
Liquidity, 1 h @ 38°C, %	96.1
Distillation, % to 235°C	0.0
235 to 300°C	15.4
% to 355°C	74.0
Coke residue, %	1.0

Table 9 - Product yields and analyses - autoclave experiments using anthracene oil as solvent

Anthracene solvent 75 mL + 0.075 mol additive
Coal sample size 7.5 g
Temperature 350°C

Additive	THF Insoluble Material							
	Mass (g)	Coal Conversion (% daf)	Analysis					
			C	H	N	O	S	Ash*
None	4.33	43.8	72.26	3.28	1.47	6.11	2.05	14.83
Piperidine	5.93	20.8	71.65	3.92	1.86	5.14	2.77	14.66
Pyridine	4.18	46.0	73.13	3.45	1.57	6.08	2.00	13.77
3,5-Lutidine	4.01	48.4	70.76	3.41	1.52	6.05	2.06	16.2
2-Methyl piperidine	2.12	75.6	72.91	3.86	1.82	6.08	3.40	11.93
N-Methyl piperidine	2.03	76.9	72.23	3.79	1.93	4.89	2.83	14.33
4-Methyl piperidine	5.89	21.4	65.44	3.19	1.47	4.68	3.02	22.20
N-Methyl pyrrolidine	6.90	6.9	70.12	3.57	1.71	5.16	2.86	16.58

* By difference

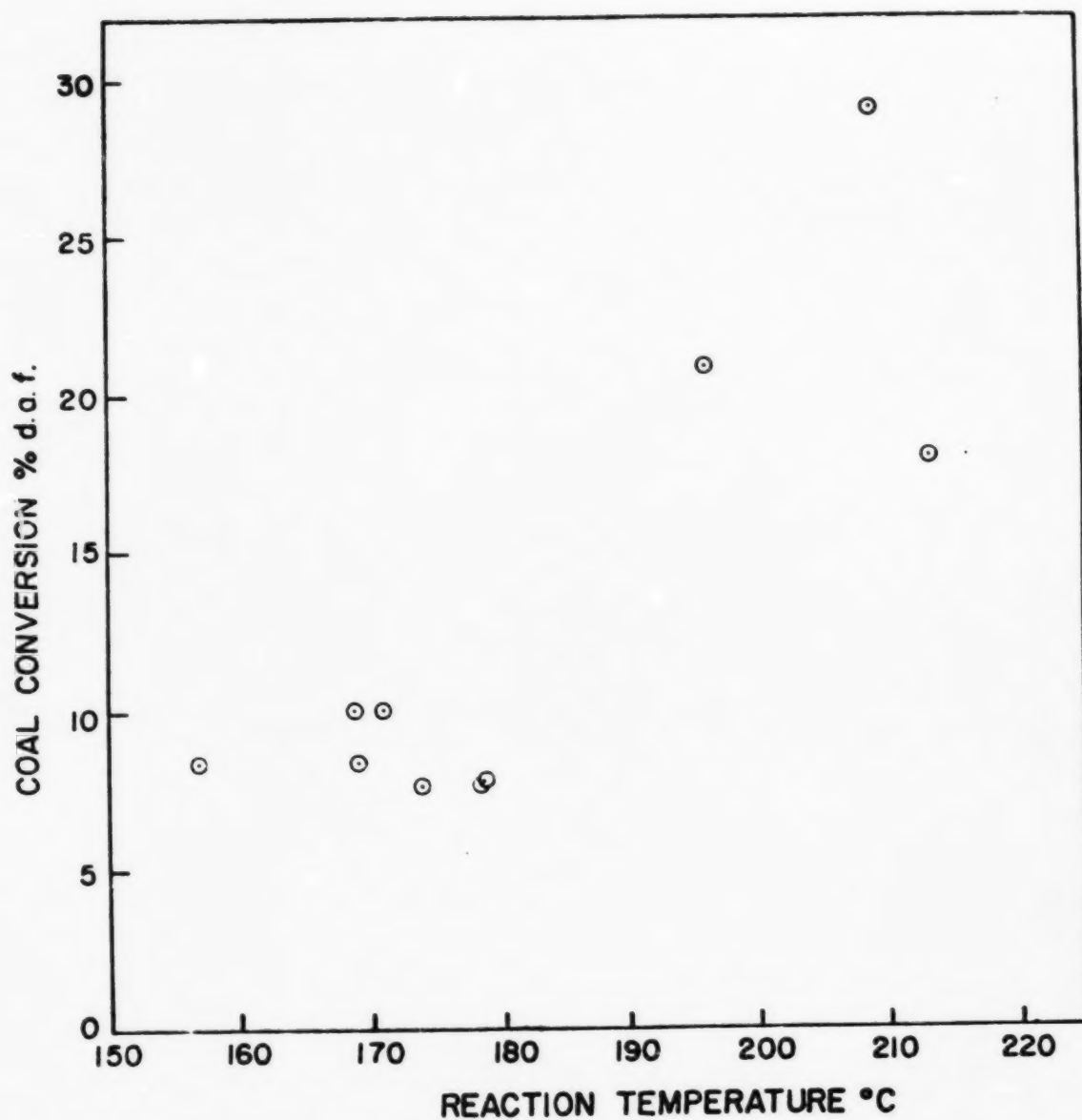


Fig. 1 - Dependence of coal conversion on reaction temperature, low pressure experiments.